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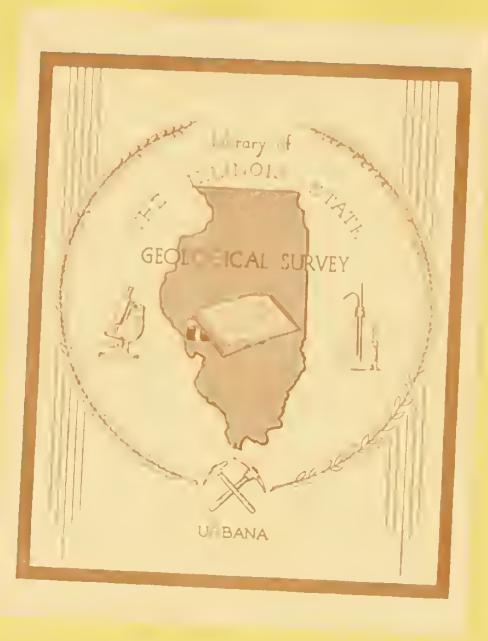
# PETROGRAPHIC PROPERTIES OF CARBONATE ROCKS RELATED TO THEIR SORPTION OF SULFUR DIOXIDE

Richard D. Harvey and John C. Steinmetz

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ILLINOIS STATE GEOLOGICAL SURVEY

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## PETROGRAPHIC PROPERTIES OF CARBONATE ROCKS RELATED TO THEIR SORPTION OF SULFUR DIOXIDE

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### ABSTRACT

Detailed petrographic, mineralogical, and chemical analyses of 26 carbonate rocks were made and compared with the capacity ( $3\frac{1}{2}$ -hr reaction period) and differential reactivity (120-sec reaction period) of calcined specimens for sorption of sulfur dioxide ( $\text{SO}_2$ ). Image analysis and scanning electron microscope methods were employed to examine limestones, dolomites, and several other types of carbonates and their calcines. A wide range of petrographic and  $\text{SO}_2$  sorptive properties was revealed.

Three petrographic and chemical properties appear to be useful indexes of the  $\text{SO}_2$  sorption capacity: the pore volume, the grain size, and the sodium oxide content of the rocks. The larger the pore volume (determined by image analysis of polished sections of limestones and dolomites) the greater was the sorption capacity of the rock. Pores with a maximum chord length of between 2 and 16  $\mu$  appear to have the most influence on sorption behavior. In general, the finer the grain size of the rock, the higher was the sorption capacity. The fine-grained, dense, limestones, however, depart from the trend and have unusually low capacities. Of the chemical elements analyzed, only sodium showed a correlation with the  $\text{SO}_2$  test data. The higher the sodium content in the samples the greater was the sorption capacity.

Unlike the sorption capacity tests, the differential reactivity tests showed little or no correlation with petrographic and chemical properties.

The reaction products of the samples calcined at 980° C for 2 hours and exposed to sulfur dioxide in laboratory tests are solid grains of anhydrite ( $\text{CaSO}_4$ ). Electron microscopy revealed two types of behavior. In calcines of Iceland spar calcite, sulfur was absorbed on the outer surface of the particles, whereas in calcines of a porous limestone, absorption took place throughout the particles. Sulfation occurred on the outer surfaces of particles by multiple nucleation of anhydrite crystallites, which enlarged until they abutted each other and produced a tightly interlocking texture of subrounded grains.

## INTRODUCTION

Air pollution caused by emission of sulfur oxides from power plants is a major environmental concern, especially in highly industrialized areas. One of the current areas of research on this problem concerns the use of limestone and related materials to react with sulfur dioxide ( $\text{SO}_2$ ) and prevent its emission. The limestone process, if it can be shown to be technically feasible, is of considerable importance because it involves the lowest capital and operation costs of any prospective process for  $\text{SO}_2$  control.

The basic procedure for this method of  $\text{SO}_2$  control is injection of pulverized carbonate rock, composed chiefly of calcite ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), into a high-temperature zone of a coal-fired boiler, where it is converted to lime ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ). The lime then combines with  $\text{SO}_2$  and oxygen ( $\text{O}$ ) released from the coal to form anhydrite ( $\text{CaSO}_4$ ), which is removed as solid particles from the flue gases.

The study reported here was made to determine the basic mineralogic and petrographic reasons for the wide variation in  $\text{SO}_2$  sorption that had been observed in laboratory and pilot-plant tests of various types of carbonate rocks. Phase I of the project (Harvey, 1970) involved the study and testing of a number of samples representative of a wide diversity of carbonate rocks. The samples were analyzed for their mineral and chemical components, including certain elements present only in trace amounts, and were subjected to detailed petrographic examinations. Correlations were sought between the properties noted and the results of tests of sulfur dioxide sorption obtained by the Division of Process Engineering of the Air Pollution Control Office (APCO), U. S. Environmental Protection Agency. The results of phase I showed certain correlations between the grain size, pore structure, and sodium content of the samples and the capacity of the calcined samples to absorb  $\text{SO}_2$ .

As a follow-up study, samples of commercially available crushed stone from carbonate rocks and their  $\text{SO}_2$  reactivity test data were obtained from the Division of Process Control Engineering of APCO, and were examined petrographically in the Survey laboratories. The results of this second study and discussion of their significance are presented in this report. The samples studied in phase I (Types 1 to 9) also are included in the discussion. As additional tests of pore volume and grain size distribution of some of these type samples resulted in revised data, the petrographic properties of these samples are given in tables 1 to 6.

TABLE 1—PETROGRAPHIC DESCRIPTION AND SOURCE OF SAMPLES

Sample no.	Rock or mineral classification	Distinguishing characteristics	Color	Grain shape	Degree of grain interlocking	Source of samples	
						Location	Geologic formation
1	Calcite (Iceland spar)	Nearly perfect crystals	Clear	Cleavage rhombs	None	Ec Jungs, Durango, Mexico	—
2	Calcite spar	Abundant crystal defects	Milky	Cleavage rhombs	None	Hillside mine dump, Rosiclare, Ill.	—
3	Limestone	Coarse-grained, high purity	Gray	Anhedral	High	Inequigranular; crinoid and bryozoan fossil fragments; intragranular voids abundant.	Columbia Quarry Co. mine, Val-meyer, Ill.
4	Limestone	Fine-grained, high purity	Gray	Anhedral	High	Equigranular; dense; a few veinlets occur with medium-sized grains of clear calcite.	Allied Stone Co. Quarry, Milan, Ill.
5	Dolomite	Reef type, high purity	Gray	Anhedral	High	Recrystallized granular; porous; abundant intragranular voids.	Midway Stone Quarry, Osborne, Ill.
6	Dolomite	Nonreef type, clayey and silty	Buff	Anhedral & rhombic	Low	Equigranular; microporous; grains adjacent to pores are rhombic. Clay along bedding planes; iron oxide along dolomite grain boundaries.	Abandoned quarry near Bourbon-nais, Ill.
7	Magnesite	Fine-grained, high purity	Milky	Anhedral & rhombic	Low	Equigranular and microporous.	Red Mountain Dist., Santa Clara Co., Cal.
8	Aragonite	Oolitic and strontium-bearing	Light buff to milky	Fibrous & bladed	High	Elliptical and cylindrical remains of marine organisms abundant; very smooth exterior surfaces; most microporous.	North Cat Cay, Bahama Islands
9	Dolomite	Limonite- and calcite-bearing	Brown & gray	Anhedral & rhombic	Low	Equigranular and microporous; rhombic grains along pores; fibrous limonite (?) occurs along dolomite grain boundaries; abundant intragranular voids.	Jeffrey Limestone Co. Quarry, Parma, Mich.

TABLE 2—MINERALOGY OF TYPE SAMPLES IN WEIGHT PERCENTAGE

Sample	Major component (%)	Minor and trace components	Insoluble residue (%)
Type 1	100 calcite	None detected	0.0
Type 2	100 calcite	Traces of soluble salts of Cl and $\text{SO}_3$	0.1
Type 3	91 calcite	8% dolomite and < 1% limonite	0.2
Type 4	98 calcite	< 2% quartz	0.9
Type 5	99 dolomite	< 1% calcite; approximately 0.3 mole % $\text{FeCO}_3$ is present in the dolomite	0.1
Type 6	81 dolomite	9% quartz; 4% calcite; 5% clay; approximately 0.8 mole % $\text{FeCO}_3$ is present in the dolomite	14.4
Type 7	99 magnesite	< 0.5% quartz and clay; approximately 0.26 mole % $\text{FeCO}_3$ and 4.51 mole % $\text{CaCO}_3$ are present in the magnesite	0.1
Type 8	96+ aragonite	Approximately 3% Mg-calcite and < 1% clay; approximately 1.38 mole % $\text{SrCO}_3$ is present in the aragonite	0.4
Type 9	70 dolomite	18% calcite; 4% quartz; < 2% clay; 5% limonite	4.2

#### Samples and Methods

Seventeen commercially available carbonate rock samples were examined and studied during this phase of the project. Included in these samples are five poorly lithified, unconsolidated, calcite-rich marls and chalks, a calcitic marble, six limestones, and five dolomites. All the limestones and dolomites contain more than 93 percent carbonates. One of the samples (2061) was the limestone injected into unit 10 of the Shawnee Steam Plant during the Tennessee Valley Authority's dry limestone injection tests.

TABLE 3—CHEMICAL ANALYSES IN WEIGHT PERCENTAGE  
(Analyses by Analytical Chemistry Section of the Illinois State Geological Survey)

Oxides	Sample type number								
	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	ND <sup>a</sup>	ND	ND	1.53	0.03	11.8	0.47	0.19	5.88
TiO <sub>2</sub>	ND	ND	ND	ND	ND	0.02	ND	ND	0.15
Al <sub>2</sub> O <sub>3</sub>	ND	0.01	ND	0.01	0.02	1.77	0.08	0.27	0.69
Fe <sub>2</sub> O <sub>3</sub>	ND	0.19 <sup>c</sup>	0.20 <sup>c</sup>	0.31 <sup>c</sup>	0.34 <sup>c</sup>	0.13	ND	ND	2.82
FeO	0.13	—	—	—	—	0.41	0.07	0.01	1.75
MnO	ND	0.06	0.10	0.09	0.02	0.02	ND	ND	0.21
MgO	ND	ND	1.86	ND	21.40	17.4	44.2	ND	15.33
CaO	55.3	55.5	53.4	54.8	30.30	26.5	2.93	55.2	30.82
Na <sub>2</sub> O	0.003	0.015	0.015	0.047	0.008	0.040	0.026	0.53	0.16
K <sub>2</sub> O	0.02	0.02	0.02	0.04	0.03	0.90	0.03	0.03	0.22
P <sub>2</sub> O <sub>5</sub>	trace <sup>b</sup>	—	—	—	—	0.02	trace	0.01	0.10
CO <sub>2</sub>	43.95	43.35	43.75	43.35	47.30	40.27	50.96	42.10	40.68
SO <sub>3</sub>	0.01	0.17	0.20	0.15	0.13	0.03	0.01	0.37	0.42
SrO	0.014	0.002	0.009	0.019	0.019	0.04	0.01	0.10	0.04
Cl	ND	0.04	0.03	ND	0.09	trace	ND	0.24	ND
Ign. loss	43.49	43.15	43.67	43.15	47.24	40.46 <sup>d</sup>	51.56 <sup>e</sup>	43.33	41.85

<sup>a</sup> ND - not detected: Limits of detection for SiO<sub>2</sub>, 0.03; TiO<sub>2</sub> and MnO, 0.01; Al<sub>2</sub>O<sub>3</sub>, 0.05; Fe<sub>2</sub>O<sub>3</sub>, 0.01; MgO, 0.10; Cl, 0.02.

<sup>b</sup> Trace of P<sub>2</sub>O<sub>5</sub>, approximately 0.005%.

<sup>c</sup> Percentage of total iron expressed as Fe<sub>2</sub>O<sub>3</sub>.

<sup>d</sup> Includes 0.3% H<sub>2</sub>O<sup>+</sup>.

<sup>e</sup> Includes 0.61% H<sub>2</sub>O<sup>+</sup>.

The samples consist of crushed particles, most of them less than an eighth of an inch in diameter, that are considered representative of a commercial product. Mineral composition of representative sample splits was determined by HCl residue and X-ray diffraction tests and by microscope observations. The samples also were subjected to chemical analysis and petrographic studies. For the petrographic studies, a large number of particles, 12 to 16 mesh, from each sample were cast in from two to six epoxy molds. Thin sections and polished specimens were prepared from the molds and analyzed. A number of particles selected from each sample were examined with a scanning electron microscope.

TABLE 4—TRACE ELEMENT<sup>1</sup> ANALYSES OF CARBONATE ROCKS DETERMINED BY NEUTRON ACTIVATION METHODS

(Analyses by Dr. R. R. Ruch of the Analytical Chemistry Section of the Illinois State Geological Survey)

Sample type	Element (ppm)									
	Cu	Br	La	Sc	Eu	As	Ga	Cr	Hg	
1	15	≤ 2	< 0.3	0.03	< 0.03	2	< 1	< 2	0.06	
2	44	< 2	3.3	0.35	5.2	≤ 2	< 7	< 11	0.06	
3	≤ 7	≤ 3	1.6	0.16	< 0.07	2	< 2	≤ 5	0.06	
4	< 3	17	< 1	0.10	< 0.2	— <sup>a</sup>	< 6	< 2	0.04	
5	11	≤ 1	1.2	0.23	< 0.05	≤ 0.8	< 2	< 4	0.03	
6	≤ 25	≤ 5	9.6	1.4	< 0.3	≤ 4	< 6	35	0.07	
7	≤ 8	< 0.9	< 0.2	0.06	< 0.1	< 0.7	< 3	127	0.03	
8	— <sup>b</sup>	17	< 1	0.05	— <sup>b</sup>	— <sup>a</sup>	— <sup>b</sup>	≤ 12	0.02	
9	25	≤ 1	3.4	1.0	< 0.7	≤ 2	< 14	≤ 31	0.23	

<sup>a</sup> Not determined, excessive interference from Br.

<sup>b</sup> Not determined, excessive interference from Na.

The grain sizes of the limestone, marble, and dolomite samples were determined from the thin sections; 300 to 700 grains were measured from each sample. Standard point-counting methods were used to select the grains for measurement. The measurements were grouped into eight to ten logarithmic size intervals (phi units, where  $\text{phi} = - \log_2 D$  and D is the apparent diameter in millimeters). These grain size measurements were corrected, according to the Rose (1968) method, for cross-section effects.

Grain size measurements of the marls and chalks were made from electron micrographs. As the diameters were determined predominantly from whole grains, no corrections for cross-section effects were deemed necessary. Cumulative percentile curves and histograms of the data from each sample were drawn. The graphic mean, equal to a third of the sum of the 16th, 50th, and 84th cumulative percentiles of the distribution (Folk and Ward, 1957), and the arithmetic mean (Krumbein and Pettijohn, 1938, p. 240) were calculated. The percentiles were determined by linear interpolation between the cumulative data points by computer methods.

TABLE 5—QUANTIMET ANALYSES OF PORE STRUCTURE OF PHASE I SAMPLES\*

Sample type	Mean pore volume (mm <sup>3</sup> /g)	Pore projection (mm)	Pore volume distribution† (mm <sup>3</sup> /gram)						Predominant occurrence of pores‡	
			0.9-2	2-2.8	2.8-3.9	3.9-5.5	5.5-7.8	7.8-11	11-16	
1	1.4	0.03	0.7	0.1	0.1	0.2	0.1	0.0	0.1	0.0
2	8	0.18	4.1	1.6	0.6	0.6	0.4	0.3	0.1	0.0
3	30	0.38	13.7	4.7	2.8	2.5	2.1	1.4	1.2	0.5
4	13	0.45	8.2	3.2	1.0	0.4	0.2	0.0	0.0	0.0
5	24	0.72	13.5	5.3	2.4	1.6	0.7	0.3	0.1	0.1
6	54	0.99	21.6	9.4	6.0	7.0	4.4	2.8	1.7	0.1
8	18	0.22	6.2	3.0	1.7	2.2	1.8	0.9	0.9	0.2
9	63	0.79	18.8	8.1	5.9	8.5	7.5	5.4	4.5	1.3

\* Image analyses of pores larger than 0.9 μ (Quantimet magnification 1300X) exclusive of type 7.

† The intervals, in microns, corresponds to a constant interval of 1/2 phi units.

‡ Determined by scanning electron microscopy.

TABLE 6—GRAIN SIZE DISTRIBUTION

Size interval ( $\mu$ )	Sample:	Frequency of grains (%)						
		Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9
1000-4000		5.8	0	3.2	0	0	0	0
500-1000		26.7	0.3	5.7	0	0	0	0
250-500		19.4	2.0	6.7	0	0	0	2.3
125-250		9.2	0.9	32.4	0	0	0.4	0.5
63-125		9.8	1.2	13.8	11.9	0	1.7	2.2
32-63		4.8	0.2	30.0	7.4	0	2.4	6.7
16-32		6.6	0.7	7.5	49.6	0.6	4.5	44.7
8-16		9.2	11.9	0.5	21.2	13.2	4.2	29.6
4-8		7.1	46.1	0.3	9.5	44.2	3.3	11.4
1-4		1.3	36.7	0.1	0.4	42.0	83.5	2.6
Mean (arith.* ) $\mu$		31.6	4.2	69.0	16.7	4.0	2.8	13.1
Mean (graphic†) $\mu$		138.0	4.1	101.0	20.0	4.0	2.3	16.0
Graphic standard deviation* (log units)		2.6	1.2	1.4	1.2	1.1	1.2	1.0

\* Krumbein and Pettijohn (1938, p. 240).

† Folk and Ward, 1957.

The pore volume and pore distribution were determined from the polished sections in vertical reflected light with a Quantimet.\* There was good contrast between the highly reflective solid areas and the nonreflective pore areas of the specimens. Negligible plucking of grains was observed and was attributed to the polishing methods. Details of the method of analysis are given in Harvey and Steinmetz (in press). To obtain statistically representative test results, 30 to 90 areas within individual particles in each sample were analyzed with the Quantimet. The area analyzed in each field of view was 0.195 mm by 0.136 mm. The magnification used (X1300) provided a resolution of 0.9  $\mu$ . Therefore, measurements were made of only those pores whose chord length was 0.9  $\mu$  or larger. To distinguish this type of measurement from the total pore volume, the term QTM pore volume is used. The means of the various measurements from each area were computed and considered to be representative pore parameters for the samples.

## RESULTS

### Petrographic Descriptions

Petrographic descriptions and source of the samples are given in table 7. Typical photomicrographs of the samples as they were observed under polarizing and scanning electron microscopes are shown in figures 1 to 3.

#### *Limestones, Dolomites, and Marble*

Limestone samples 1343 (fig. 1) and 2060 are very similar, being high-purity, fossiliferous, fragmental rocks with a micritic type of calcite matrix that is very fine grained (2  $\mu$  to 8  $\mu$ ), dense, and anhedral. The fossil fragments consist of interlaminated grains of calcite (brachiopods), large single crystalline grains of calcite (crinoid fossil plates), and fine-grained calcite (other remains of marine invertebrates). Abundant patches of sparry and anhedral calcite grains occur in former fossil voids and in other irregular areas in the rock (fig. 1, 1343). In some fragments the sparry calcite has replaced parts of the original fossil material.

Sample 2061 (fig. 1) is a soft, oolitic, porous limestone. The oolites are mainly of a normal type in that they consist of spherical or ellipsoidal bodies 0.5 to 1 mm across with a nucleus and concentric rings. Most nuclei are single crystals of calcite (crinoid fossil fragments); rarely, they are quartz sand grains. The concentric rings consist of very fine-grained calcite. The rings can be seen in sample 2061 (fig. 1), poorly defined by the dark bands, shown magnified 30 times (X30), and in the center area of the same sample at 430 magnification (X430). Few of the oolites have radial structure in their outer rings. Many superficial oolites occur that have only one ring around the nucleus. Several oolites in 2061 are flattened, and others have deformed or ruptured outer rings. Fossils occurring in 2061 are mainly crinoid, brachiopod, bryozoan, and ostracode fragments. Irregularly shaped,

\* An image analyzing computer (Quantimet, model B) manufactured by Metals Research Limited, Melbourn, England. A petrographic microscope is a major component of this instrument.

EXPLANATION OF FIGURE 1

1343 — TPL (Thin-section in transmitted crossed-polarized light); shows inequigranular and fossiliferous nature of the limestone. A foraminifera test is shown in the lower left and clear sparry calcite is scattered throughout the fine-grained calcite. The dark grains, near center and in upper left, are calcite oriented at optical extinction in crossed-polarized light.

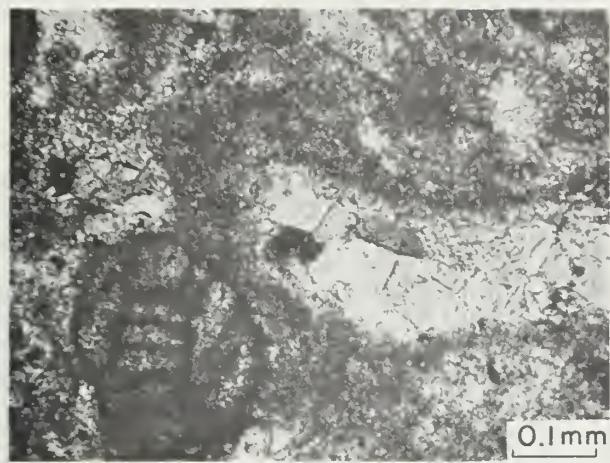
1359 — SEM (Fracture surface in scanning electron microscope); shows equigranular character of the limestone sample and high degree of grain-interlocking.

2061 — TPL; shows oolitic and fossiliferous nature of the limestone. The dark areas are very fine grained and the light areas are medium- to coarse-grained (crinoid fossil fragments) sparry calcite.

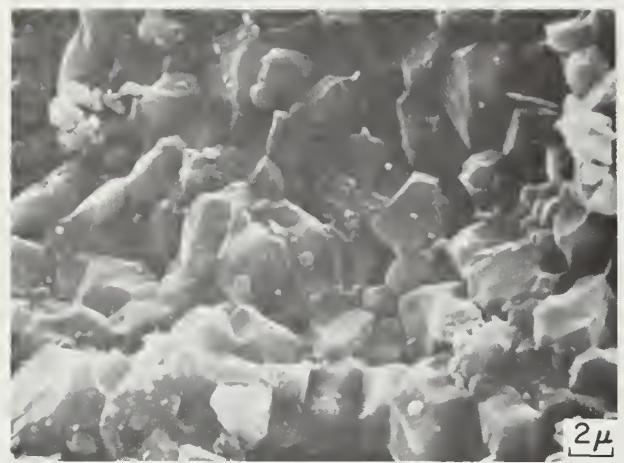
2061 — SEM; shows detail of the main components in the limestone: (1) large single crystal grain of calcite (crinoid fossil fragment) with intracrystalline voids on left, (2) very fine-grained and poorly interlocking calcite grains that form the outer bands of the oolites and fossil fragments (see 2061-TPL), and (3) the medium-sized and tightly interlocked grains of clear sparry calcite on the right.

2065 — TPL; shows the inequigranular character of the irregular patches of sparry calcite. SEM photographs of the pelletoids that occur in this sample appear as in 1359 above. The dark grains are mainly crystalline grains of calcite oriented at optical extinction and a few grains of opaque pyrite.

1336 — SEM; shows cleavage surface of a large grain of calcite in the marble. Note the presence of eight voids, approximately 0.5 to 2 microns across, shown in this micrograph.

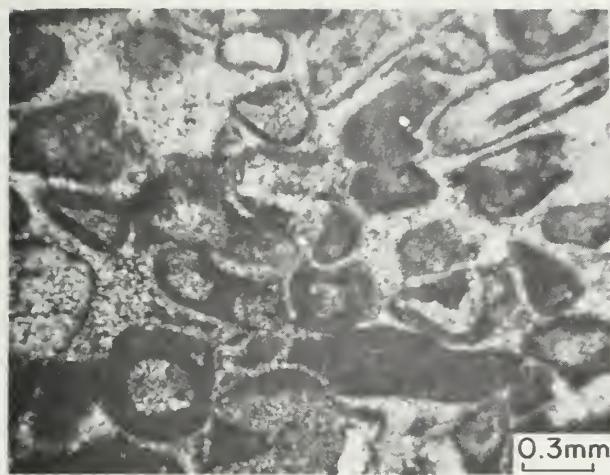


1343 - Limestone



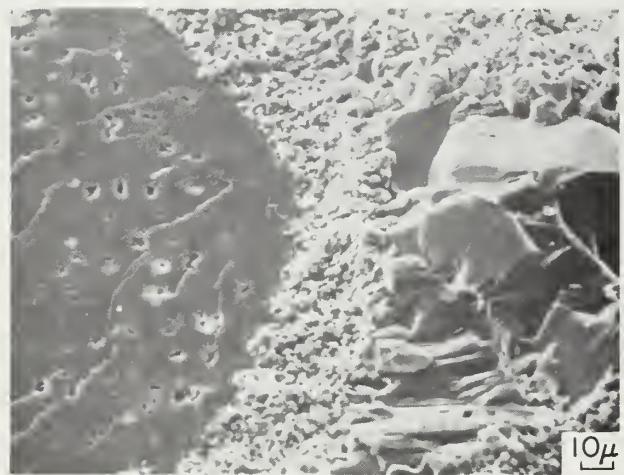
1359 - Limestone

X3310



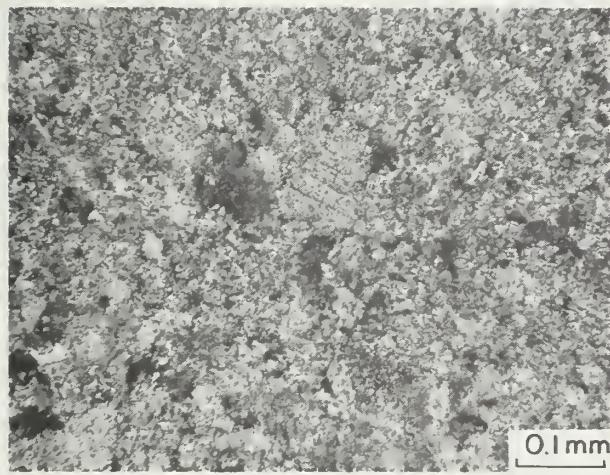
2061 - Limestone

X30



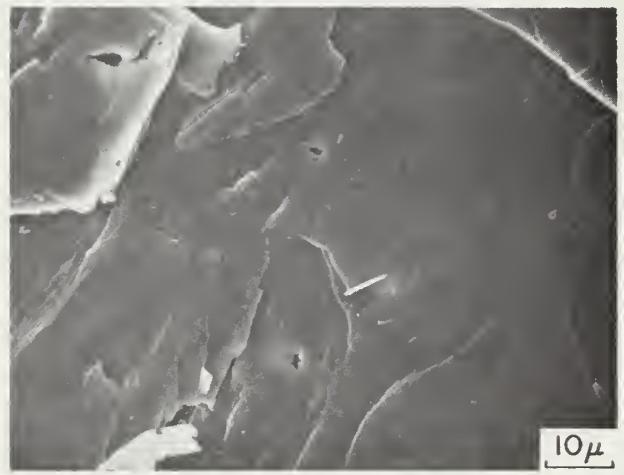
2061 - Limestone

X430



2065 - Limestone

X130



1336 - Marble

X990

Fig. 1 - Typical textures and grain characteristics of limestones and marble.

TABLE 7—PETROGRAPHIC DESCRIPTION AND SOURCE OF SAMPLES

Sample number	Granularity	Relative grain size	Grain shape	Degree of grain interlocking	Other textural features	Source
<u>LIMESTONES</u>						
1343	Inequigranular	Fine to medium	Anhedral	High	Micro-fossiliferous and fragmental: algal, foraminifera, brachiopod shells etc., also pelletoidal.	Hooper Bros., Weeping Water, Nebraska (1/8" down aglime)
1359	Equigranular	Fine	Anhedral	High	Few veinlets of medium-grained sparry calcite. Few specimens are inequigranular, others limonite bearing.	Grove Lime Company, Stephens City, Virginia (aglime)
2060	Inequigranular	Fine to coarse	Anhedral	Moderate	Fossiliferous and fragmental; abundant coarse crinoid plates, other fine-grained fossils (see 2061), dolomite and quartz silt (24 $\mu$ ) set in very fine calcite matrix.	Fredonia Valley Quarri Fredonia Valley, Kentucky (Blue Ledge)
2061	Inequigranular	Fine and coarse	Anhedral - subhedral	Low	Oolitic and fossiliferous and fragmental: fine-grained brachiopods, echinoids, bryozoans, ostracods, and foraminifera fragments; and few coarse single grained crinoid plates.	Fredonia Valley Quarri Fredonia Valley, Kentucky (Upper white ledge)
2065	Inequigranular	Fine to medium	Anhedral	Moderate	Pelletoidal, with sparry calcite (10 $\mu$ ) cement; also irregular patches of medium-grained sparry calcite.	Longview Limestone (TVA)
2071	Inequigranular	Very fine and medium	Anhedral and rhombic	High	Mostly very fine-grained even textured with scattered dolomite rhombs throughout the stone particles. Few patches of sparry calcite in some specimens.	Marble Cliff, Carntown Kentucky (TVA)
<u>MARBLE</u>						
1336	Single crystal particles	Very coarse	Cleavage rhombs			Georgia Marble Company Tate, Georgia (#2 crushed marble)

Sample number	Granularity	Relative grain size	Grain shape	Degree of grain inter-locking	Other textural features	Source
<u>DOLOMITES</u>						
1337	Equigranular	Coarse	Rhombic	High	Granular mosaic, microporous; few specimens are fine-grained.	Chas. Pfizer Company, Gibsonburg, Ohio (#10 Glasshouse stone)
1378	Inequigranular	Coarse, medium and fine	Sub-rhombic	High	Granular mosaic; grain boundaries tend to be stairstepped in many particles, others are curvilinear.	Verplanks Coal and Coke Company, Fettysburg, Michigan (Fluxing fines)
1380	Equigranular	Medium	Sub-rhombic	High	Granular mosaic; grain boundaries tend to be stairstepped.	Rockwell Lime Company, Manitowoc, Wisconsin
1688	Inequigranular	Coarse and medium	Rhombic	High	Granular mosaic	Marblehead Lime Company, Chicago, Illinois
2069	Equigranular	Medium and fine	Rhombic and anhedral	High	Mixture of fine-grained (anhedral) and medium-grained (rhombic) stone particles.	James River Limestone, (TVA)
<u>MARLS AND CHALKS</u>						
2080	Inequigranular friable	Fine	Anhedral and fibrous	Moderate	Banded algal (?) structures and foraminifera, also globular and irregular shaped agglomerates. Sparry calcite cement partly surrounding banded particles. The latter crystallites are generally parallel to one another (fibrous).	Ohio Geological Survey Columbus, Ohio (NE, OH)
2109	Inequigranular friable	Fine	Anhedral	Low	Variety of thin fossil shells and other microfossils and woody organic matter. Thin bands of organic-rich matter surround many dense very fine-grained calcite globules. Also some specimens with abundant quartz silt (20-50 $\mu$ ). Pores largely in microfossil cavities. Scattered limonite grains.	Soil Conservation Service, Syracuse, New York (Canastota, Madison County, New York)

TABLE 7—PETROGRAPHIC DESCRIPTION AND SOURCE OF SAMPLES (Concluded)

Sample number	Granularity	Relative grain size	Grain shape	Degree of grain interlocking	Other textural features	Source
2129	Equigranular friable	Fine	Anhedral	Low	Predominantly fine, even textured calcite ( $1\ \mu$ ); few scattered thin shelled fossils and limonite-organic-rich particles and stringers. Few scattered quartz grains up to 1 mm diameter.	S. K. Vorres, R. R. 2, Fremont, Michigan (Newaygo County, Michigan)
2077	Inequigranular friable (Austin chalk)	Fine	Anhedral	Low	Sparry calcite (up to 15 mm across) fossil materials scattered sparsely throughout a very fine-grained (micritic) calcite. Few green glauconite clay pellets and limonite-rich particles.	Longhorn Portland Ceme San Antonio, Texas (Austin chalk)
2081	Inequigranular friable (Kansas chalk)	Fine	Anhedral and fibrous	Moderate	Abundant foraminiferal tests (up to 0.5 mm across) consisting of very fine-grained calcite and medium-grained calcite spar filling voids in the tests. Also banded algal (?) structures, alternating very fine and medium-grained (fibrous) calcite (5-15 $\mu$ ). Some specimens mainly pelletoidal. Scattered quartz silt (10-25 $\mu$ ) and limonite. Few soft gray clay particles.	State Geological Survey Lawrence, Kansas (Kansas chalk)

fine-grained intraclasts also are present. The oolites, fossils, and intraclasts are cemented together by clear, sparry, anhedral calcite (light colored areas surrounding oolites in fig. 1, 2061, at X30; also shown on right side of 2061 at X430).

Sample 1359 (fig. 1) is a very fine-grained, even-textured, dense limestone that is almost entirely micritic calcite. This limestone is essentially the same as Type 4 of phase I. The high degree of grain interlocking and the character of the grains can be seen in the figure.

Sample 2065 (fig. 1) is a pelletoidal limestone. It consists predominantly of ellipsoidal pellets as much as 0.5 mm across that consist of a mixture of micritic and sparry calcite. In figure 1, detail of the interior structure of a pellet is visible. The pellets are surrounded by sparry calcite.

Sample 2071 is dominantly micritic calcite (similar to 1359); however, rhomb-shaped crystals of dolomite, 35  $\mu$  to 40  $\mu$  in size, are scattered throughout the rock.

The marble, sample 1336 (fig. 1), is uniformly very coarse-grained calcite spar, and the crushed sample consists almost entirely of cleavage rhombs or irregularly broken fragments of a single crystal of calcite. Scattered through the particles are a few grains of tremolite (ideal composition:  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), a mineral commonly associated with marble. Few intragranular voids or inclusions were observed in specimens of the marble with the SEM.

The dolomite samples described in table 7 also are petrographically very similar. They are all more than 98 percent dolomite, and each appears to have a similar geologic origin—replacement of original limestones. Their textures, resulting from the replacement and recrystallization processes, are similar (fig. 2), and they differ mainly in grain size distribution and pore structure. Samples 1378 and 2069 (fig. 2) are less equigranular than the other samples, and 1337 (fig. 2) has the highest porosity. With the exception of 1337, the samples are very similar to sample Type 5 of the phase I study (table 1).

#### Marls and Chalks

The marls and chalks (fig. 3) are grouped together because the samples of these two types of carbonate rocks are similar in mineralogy and texture. Marl is defined as a "semifriable mixture of clay materials and lime carbonate" (Pettijohn, 1957, p. 369). The mineral composition of marls varies greatly, and various limits of the carbonate and clay contents have been proposed, ranging from 25 to 75 percent carbonate and a complementary content of clay (Gillson, 1960). Quartz silt and organic matter are usually present, and, in some deposits of marl, calcite occurs only in fossil shells.

Chalk is a porous, fine-textured, and somewhat friable carbonate rock. Normally, it is light buff to white and consists almost wholly of calcitic shells of microfossils (Pettijohn, 1957, p. 400). Most chalks are 90 or more percent calcite, although, according to Gillson (1960), rocks that are classified as chalks may be as much as 25 percent noncalcite.

EXPLANATION OF FIGURE 2

1337 — TPL; equigranular and coarse-grained dolomite. Dark grains oriented at optical extinction show very small crystallite inclusions. Several grains show characteristic rhombic angles by intersection of grain boundaries.

1378 — TPL; inequigranular dolomite showing few occurrences of "stairstep" grain boundaries. The dark inclusions abundantly shown in the grains are intragranular voids such as are shown in the SEM photograph of 1688 below. The larger dark areas are dolomite grains.

1380 — TPL; equigranular dolomite showing typical granular mosaic. Grain boundaries tend to be less linear than those in the other samples. Note also the abundance of very small and dark-appearing inclusions (voids) within the grains.

1688 — TPL; inequigranular dolomite.

1688 — SEM; shows detail of the type of intragranular voids common in all of the dolomite samples.

2069 — TPL; mosaic of equigranular dolomite.

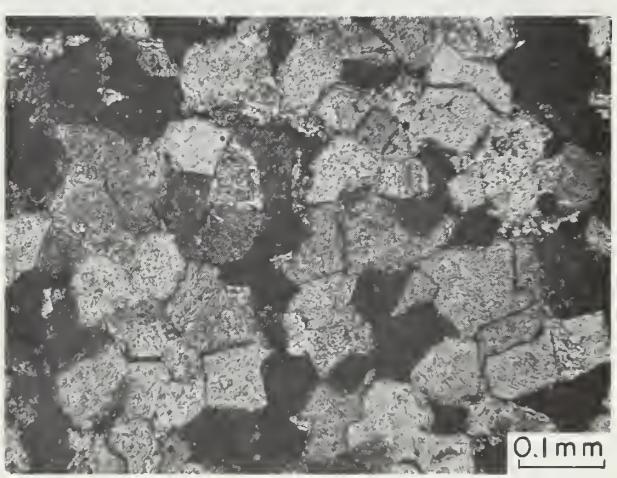
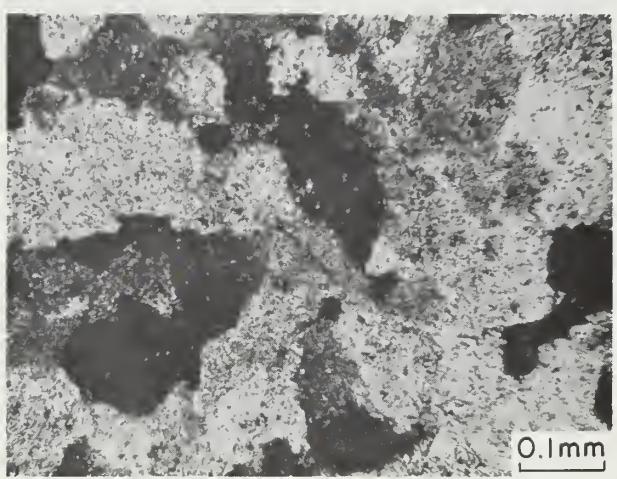
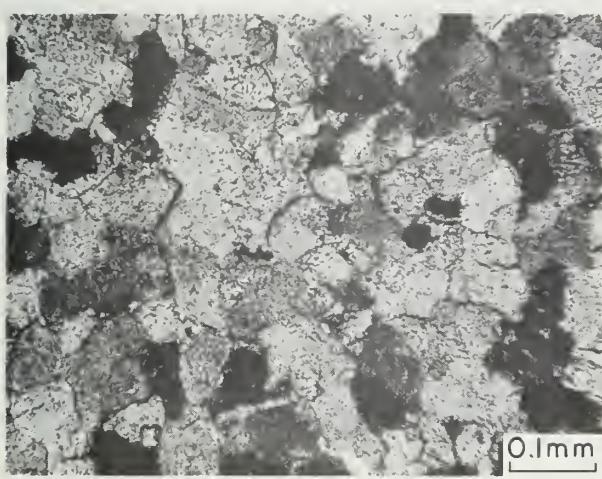
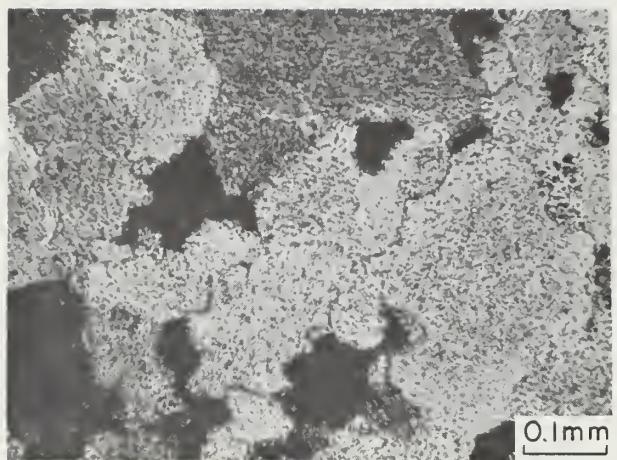
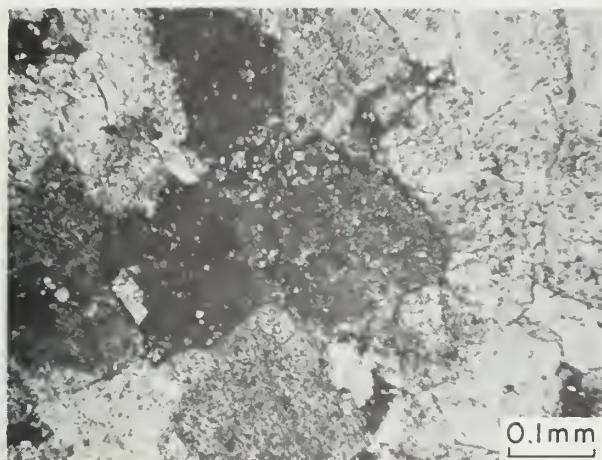


Fig. 2 - Typical textures and grain characteristics of dolomites.

EXPLANATION OF FIGURE 3

2080 — SEM; shows fine-grained, partly fibrous, and porous character of the marl.

2109 — SEM; shows general texture of the marl. Note the uniformity of grain sizes compared with those of 2080.

2129 — SEM; shows the fine-grained and agglomerated character of the marl (X2800).

2129 — SEM; close-up view of one agglomerate particle showing the platy crystallites of calcite and the highly porous nature of the particle.

2077 — SEM; shows the granular nature of the chalk. The particles are single subrhombic grains 1 to 2  $\mu$ , or agglomerates of interlocking grains whose porosity appears to be less than that of those in 2129.

2081 — SEM; shows the character of the chalk. Note the presence of fibrous particles of calcite and the polygranular nature of the particles.

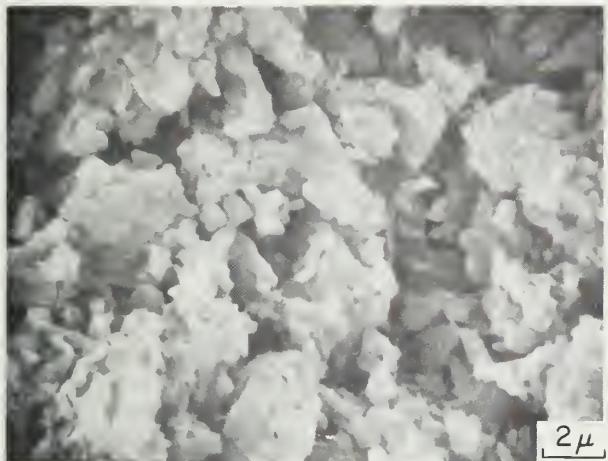


2080 - Marl



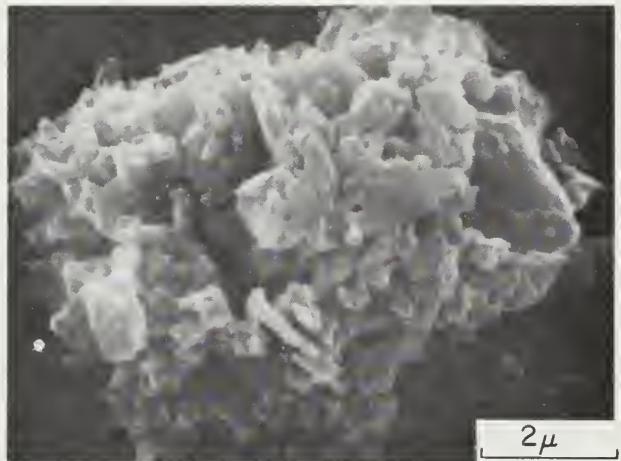
2109 - Marl

X2400



2129 - Marl

X5000



2129 - Marl

X10,000



2077 - Chalk

X5100



2081 - Chalk

X5600

Fig. 3 - Typical textures and grain characteristics of marls and chalks.

Most literature on the deposition of fresh-water lake marls of New York through Minnesota describes the importance of an alga (*Chara*) that causes  $\text{CaCO}_3$  to precipitate on its surfaces. The carbonate, as very fine-grained calcite, is eventually sloughed off the alga and accumulates on the bottom of the lake, where it forms marl.

The samples of marl and chalk studied in this phase are described in detail in table 7, and typical electron micrographs are shown in figure 3. The samples are composed of a variety of microfossils, mainly shells (up to 0.5 mm) of foraminifera, plus a few gastropod shells and other fossil remains. The Kansas chalk (2081) and Ohio marl (2080) are petrographically very similar, as is shown in table 7 and figure 3. Marls (2109 and 2129), and the Austin chalk (2077) also are similar, although the Austin chalk contains more coarse sparry calcite than the marls. All the chalks and marls investigated here are characterized by their high calcite content, poor consolidation, high porosity, and very fine grain structure.

#### Grain and Pore Size Distributions

The results of grain size measurements (table 8) indicate the limestones are predominantly fine grained. Sample 2060 is the only limestone that does not have a major mode at approximately 2 microns. The dolomites are much coarser than the limestones and show a wider range of major modes. However, four of the five dolomites have a graphic mean near 120 microns. The fifth dolomite (2069) has a mean of 53 microns.

The marls and chalks are the finest grained samples and, of these, the Michigan marl (2129), with a graphic mean diameter of 0.4 microns, is the finest grained. The Kansas chalk (2081) is the coarsest of this group, having a graphic mean diameter of 1.6 microns. Thin sections of these rock samples show a few small areas in which grains up to 0.3 mm across occur. These relatively large grains represent a negligible fraction in each of these samples.

The results in volumetric units\* of the pore volume studies made with the Quantimet on epoxy-cast specimens (table 9) show this technique of analysis is applicable to consolidated rocks. It makes possible the measurement of isolated pores and intragranular (intracrystalline) voids. The QTM pore volume measurements are slightly higher than the "water immersion" type of porosity measurements for a few of the samples that were subjected to such porosity tests. As the immersion tests give values lower than the true porosity by an amount equal to that of the isolated pores or voids occurring within the solid specimen, the QTM measurements of pores whose chord length is greater than  $0.9 \mu$  are considered essentially equal to the true, or total, pore volume of the limestone, dolomite, and marble. However, the results from two of the

\* As the pore volume in  $\text{cm}^3/\text{gram}$  is equal to the pore volume ( $p$ ) expressed as a decimal fraction divided by the bulk density in  $\text{gram}/\text{cm}^3$ , the pore volume in  $\text{mm}^3/\text{gram}$  is given by

$$V = 10^3 p / (P_g(1-p))$$

where  $P_g$  is the density of the mineral grains in the rock specimen.  $P_g$  for calcite was taken as 2.71, dolomite as 2.85, and aragonite as 2.93.

TABLE 8—GRAIN SIZE ANALYSES

Sample	Distribution	Modes* ( $\mu$ ) major; minor	Graphic mean† ( $\mu$ )	Graphic standard deviation (in log units)	Arithmetic mean‡ ( $\mu$ )
LIMESTONES					
1343	Fine skew	2	6.2	2.0	4
1359	Bimodal	2; 20	2.7	1.2	3
2060	Irregular	20, 2; 180	12.2	2.2	7
2061	Bimodal	2; 90	10.2	2.9	5
2065	Irregular	2; 10, 45	6.2	2.2	4
2071	Fine skew	2	4.1	0.3	3
MARBLE					
1336	Normal		1300**		
DOLOMITES					
1337	Coarse skew	150	126.9	0.9	107
1378	Irregular	210, 50; 25	119.0	1.1	89
1380	Normal (with very minor second mode)	105; (25)	117.2	0.9	94
1688	Bimodal	125; 50	119.0	0.8	108
2069	Normal	50	52.9	0.8	45
MARLS AND CHALKS					
2080	Fine skew	0.8; 25	0.9	1.1	1.1
2109	Fine skew	0.8; 5	0.8	1.1	1.1
2129	Fine skew	0.4; 10	0.4	1.2	0.6
2077	Fine skew	1; 15	1.1	1.0	1.4
2081	Fine skew	2; 10	1.6	1.4	2.9

\* As observed from histogram plots of equal logarithmic size intervals.

† Folk and Ward, 1957.

‡ Krumbein and Pettijohn (1938, p. 240).

\*\* Single grained particles (12 by 16 mesh). Average grain size = average particle size = 1300  $\mu$ .

TABLE 9—QUANTIMET ANALYSES OF PORE STRUCTURE

Sample	Mean pore volume (mm <sup>3</sup> /g)	Pore projection (mm)	Pore volume distribution <sup>†</sup> (mm <sup>3</sup> /g)						Predominant position of pores <sup>‡</sup>	
			0.9-2	2-2.8	2.8-3.9	3.9-5.5	5.5-7.8	7.8-11	11-16	
LIMESTONES										
1343	22	0.22	11.7	5.1	2.4	1.8	0.6	0.2	0.1	< 0.1
1359	10	0.09	6.9	2.2	0.5	0.3	< 0.1	< 0.1	0	Between grains
2060	9	0.29	5.3	2.0	1.0	0.6	0.2	0.1	0	Between grains
2061	21	0.32	12.8	4.7	1.5	1.0	0.4	0.4	0.1	Between grains
2065	9	0.09	5.1	2.5	0.8	0.6	0.2	< 0.1	< 0.1	Variable
2071	18	0.52	12.1	3.7	1.2	0.6	0.1	< 0.1	< 0.1	Between grains
MARBLE										
1336	8	0.18	5.0	1.4	0.6	0.5	0.4	0.2	0.1	Within grains
DOLOMITES										
1337	51	0.46	30.9	11.2	4.5	4.6	3.9	1.3	1.3	0.8
1378	14	0.22	7.5	2.8	1.4	0.9	0.8	0.4	0.1	Within grains
1380	18	0.38	11.5	3.4	2.2	0.9	0.5	0.2	0.2	Within grains
1688	24	0.55	14.5	5.2	1.9	1.4	0.5	0.3	0.1	Within grains
2069	15	0.40	8.4	2.8	1.3	1.1	0.6	0.4	0.1	Within grains
MARLS AND CHALKS										
2080	21	0.42	13.9	3.2	1.0	1.4	0.7	0.4	0.3	0.2
2109	9	0.17	5.6	1.6	0.7	0.5	0.3	0.1	< 0.1	Between grains
2129	73	1.34	29.2	14.4	8.7	9.1	5.3	3.7	1.7	1.0
2077	56	0.19	28.0	14.9	6.9	4.0	1.6	0.4	0.1	Between grains
2081	17	0.36	10.8	2.8	1.4	0.9	0.6	0.3	0.1	Between grains

\* Image analyses of pores larger than 0.9 μ. Quantimet magnification of 1300X.

† The intervals, in microns, correspond to a constant interval of 1/2 phi units.

‡ Determined by scanning electron microscopy.

marls and one chalk (2080, 2109, and 2081) are anomalously low because epoxy filled some of the larger pores during the casting process. The QTM pore volume distribution (tables 5 and 9) was computed from the percentage size distribution as given in the footnote on page 20.

### Mineralogy

The mineral compositions of the samples are listed in table 10. The residues from 20-gram samples of the limestones and dolomites that were insoluble in hydrochloric acid (HCl) proved to be mainly quartz and clay in various amounts plus smaller amounts of organic matter and a grain or two of opaque minerals, mainly pyrite. Sample 2060 has the highest residue (5.92 percent) found in the limestones and dolomites. As much as 13 percent of the marls and chalks are residue. Much of the residues from 2109 and 2129 are woody organic matter. In addition, HCl-soluble organic matter occurs in the marls and chalks. The calcite ranges from 76 to 98 percent by weight in the marls.

### Chemical Analyses

The results of analyses of the major and minor elements present in the samples are listed in table 11. The data show that, of the limestone samples, 2060 contains the most  $\text{SiO}_2$  (4.42 percent) and the least  $\text{CaO}$  (49.2 percent). The composition of the dolomite mineral, as calculated from the chemical analyses, is given in table 10. The analyses indicate slightly more calcium than magnesium in all samples except 1688, which has the ideal dolomite composition ( $\text{Ca/Mg} = 1/1$ ).

Chemical analyses of the marls and chalks show they contain various amounts of organic matter and silica. Sulfur contents range from 0.01 to 0.62 percent. The sulfur occurs mainly in very rare, small grains of pyrite. Less than 0.1 percent of the sulfur in these samples is organic. In the marl from Michigan (sample 2129), sodium and water contents are high.

### DISCUSSION OF RESULTS RELATED TO SULFUR DIOXIDE SORPTION TESTS

The samples of carbonate rocks investigated were tested for their  $\text{SO}_2$  reactivity by personnel of the Division of Process Control Engineering, APCO, Cincinnati, Ohio. Two methods were used to evaluate the relative reactivity of carbonate rock samples with  $\text{SO}_2$  in flue gases. Their capacity for reaction was measured in a fixed-bed reactor (Potter, 1969), and an indirect assessment of the rate of reaction was made with a differential reactor, according to the Borgwardt (1970a) method.

For the capacity test, a weight of uncalcined sample equivalent to 20 grams of calcine, 16 to 20 Tyler mesh, was exposed in a fixed-bed reactor to a flue gas containing 2700 ppm  $\text{SO}_2$  for  $3\frac{1}{2}$  hours at  $1800^\circ \text{F}$ . The gain in

TABLE 10—MINERAL ANALYSES

Sample	Major component (%)	Minor and trace components	HCl insol residue
LIMESTONES			
1343	98 Calcite	1.4% kaolinitic clay; trace of quartz	1.65
1359	99 Calcite	Traces of illitic clay and dolomite	0.65
2060	81 Calcite	12% dolomite; 3.5% quartz; 2% illitic clay; trace of limonite	5.92
2061	98+ Calcite	< 1% kaolinitic clay; < 1% quartz sand	1.11
2065	94 Calcite	5% dolomite; trace of quartz as sand and silt; trace of clay	0.95
2071	95 Calcite	3.8% dolomite; < 1% quartz; traces of feldspar and clay	1.73
MARBLE			
1336	98 Calcite	1+ % tremolite; < 1% mica	1.95
DOLOMITES			
1337	99+ Dolomite* $Ca_{1.14}Mg_{.86}(CO_3)_2$	Traces of quartz and clay	0.34
1378	98 Dolomite $Ca_{1.03}Mg_{.97}(CO_3)_2$	1% quartz sand; < 1% clay	1.88
1380	99 Dolomite $Ca_{1.03}Mg_{.97}(CO_3)_2$	< 1% cherty quartz; < 1% clay	0.76
1688	99+ Dolomite $Ca_{1.00}Mg_{1.00}(CO_3)_2$	Traces of quartz and clay	0.35
2069	98 Dolomite $Ca_{1.08}Mg_{.92}(CO_3)_2$	1.5% kaolinitic clay; trace of limonite	1.94
MARLS AND CHALKS			
2080	98 Calcite	1% organic matter; 1% illitic clay; < 1% silty quartz	1.19
2109	92+ Calcite	5% woody and HCl-soluble organics; 2% clay; 2% dolomite	2.58
2129	76+ Calcite	11% organics, mainly woody; 3% illitic clay; 4% silty quartz; 4% dolomite	13.07
2077	87+ Calcite	6% glauconitic clay; 3% quartz; 1% limonite; trace of feldspar	8.11
2081	92+ Calcite	2% organic matter; 1% clay; 1% quartz; trace of feldspar	2.82

\* The proportions of  $Ca^{++}$  and  $Mg^{++}$  in the dolomite, calculated from analyses in table 13, are as shown. Ideal dolomite is  $Ca_{1.0}Mg_{1.0}(CO_3)_2$ .

TABLE 11—CHEMICAL ANALYSES IN WEIGHT PERCENTAGE  
(Analyses by Analytical Chemistry Section, Illinois State Geological Survey)

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	S	H <sub>2</sub> O+	CO <sub>2</sub>	Organic C	Total
<b>LIMESTONES</b>													
1343	0.11	0.57	0.14	*	*	54.8	0.031	0.06	0.04	*	43.10	*	98.8
1359	*	0.14	0.07	0.011	trace	55.5	0.007	0.01	*	0.25	43.27	0.15	99.5
2060	4.42	0.64	0.23	0.016	2.79	49.2	0.047	0.15	trace	0.26	41.58	*	100.3
2061	0.29	0.47	0.14	0.013	*	55.0	0.012	*	*	0.22	43.63	*	99.8
2065	0.25	0.04	0.28	0.009	*	55.0	0.004	0.14	0.01	*	43.48	*	99.2
2071	0.56	0.33	0.11	0.005	0.92	54.3	0.034	0.06	0.03	*	43.52	*	99.9
<b>MARBLE</b>													
1336 <sup>†</sup>	0.08	0.40	0.12	0.005	1.01	54.1	0.011	0.03	*	*	43.25	*	99.0
<b>DOLOMITES</b>													
1337	*	0.15	0.19	0.004	18.0	33.2	0.044	0.11	< 0.01	0.04	47.17	*	98.9
1378	*	0.43	0.02	*	20.82	30.7	0.066	0.01	0.01	0.01	46.42	*	98.5
1380	*	0.27	0.19	*	20.67	30.5	0.044	0.02	< 0.01	0.23	46.97	*	98.7
1688	*	0.21	0.02	*	21.57	30.0	0.048	0.01	< 0.01	1.10	47.09	0.01	101.1
2069	0.44	0.61	0.23	0.020	19.2	31.4	0.031	0.22	0.04	0.84	44.93	0.60	98.6
<b>MARLS AND CHALKS</b>													
2080	*	0.67	0.03	*	*	54.8	0.024	0.05	0.62	1.23	40.99	0.35	98.8
2109	*	0.84	0.01	*	1.88	51.7	0.033	0.02	0.55	1.47	40.16	2.77	99.4
2129 <sup>†</sup>	5.10	0.88	0.47	0.01	3.08	43.9	0.160	0.01	0.19	4.66	35.38	6.18	100.0
2077	6.34	2.17	0.82	0.01	*	49.2	0.035	0.49	0.01	1.13	38.31	0.19	98.8
2081 <sup>†</sup>	2.48	1.09	0.15	*	1.41	51.4	0.060	0.11	0.57	1.16	39.44	0.95	98.8

\* None detected.

<sup>†</sup> Mercury in 1336 = 0.19 ppm, in 2129 = 0.07 ppm, and in 2081 = 0.77 ppm; not determined in other samples.

TABLE 12—SO<sub>2</sub> REACTIVITIES  
(SO<sub>2</sub> tests by Division of Process Control Engineering, APCO)

Sample	Rock classification	Sorption capacity, fixed bed (g/20 g)	Reactivity, differential (mg SO <sub>3</sub> /30 mg calcine)
Type 1	Iceland spar (calcite)	5.46	8.3
Type 2	Calcite spar	11.65	9.6
Type 3	Limestone	10.73	13.9
Type 4	Limestone	6.97	14.0
Type 5	Dolomite	9.03	17.0
Type 6	Dolomite	13.68	12.1
Type 7	Magnesite	1.78	—
Type 8	Aragonite	18.30	7.1
Type 9	Dolomite	14.91	15.8
1343	Limestone	6.06	5.08
1359	Limestone	4.94	—
2060	Limestone	12.25	8.98
2061	Limestone	9.52	4.84
2071	Limestone	7.40	4.42
1336	Marble	7.50	3.86
1337	Dolomite	11.53	9.28
1378	Dolomite	11.90	7.08
1380	Dolomite	8.70	6.53
1688	Dolomite	11.35	—
2069	Dolomite	9.08	8.82
2080	Marl	15.60	6.60
2109	Marl	15.38	7.12
2129	Marl	14.83	14.92
2077	Chalk	12.54	8.62
2081	Chalk	13.37	11.73

weight of the sample after the test period was taken as the measure of the sample's SO<sub>2</sub> sorption capacity. The results of the fixed-bed capacity tests of the samples appear in table 12.

For the differential reactor tests, the stone was precalcined at 1800° F for 2 hours, and a 150- to 170-mesh calcine was reacted at 1800° F for various periods of time with flue gas containing 2700 ppm SO<sub>2</sub>. The plot of the amount of SO<sub>3</sub> sorbed by the sample versus time was constructed and evaluated at 120 seconds to obtain the differential reactivity. These values, supplied by the Division of Process Control Engineering, for the samples investigated also are given in table 12.

In the discussions that follow, samples of all the carbonate rocks studied are considered.

#### Petrography Related to Sorption of Sulfur Oxides

No consistent correlation is apparent between the results of fixed-bed and differential  $\text{SO}_2$  reactivities and the mineralogy of the samples. A clayey and silty nonreef type of dolomite, selected for study because of its impurity, contains about 25 percent inert oxides in its calcine, yet this sample had one of the highest  $\text{SO}_2$  capacities. On the other hand, Borgwardt (1970b) found the rate of reaction of this sample notably reduced, compared to rates of high-purity calcines, at a particular degree of sulfation. Considered in terms of capacity for sorption of  $\text{SO}_2$ , the textural properties of the calcine and, presumably, of the raw stone, outweigh a moderate degree of impurity.

In the fixed-bed capacity tests, the dolomites gained an average of 11.27 grams (of  $\text{SO}_3$ ) per 20 grams of calcine, and the limestones averaged 6.84. The marls and chalk had a high average of 14.34 g/20 g, and the oolitic aragonite (Type 8) adsorbed the largest amount of  $\text{SO}_2$  (18.3 g/20 g). The magnesite (Type 7) had the lowest sorption capacity (1.78 g/20 g). The limestones containing abundant crinoidal fossil fragments had higher  $\text{SO}_2$  sorption capacities than the other limestones. The crinoid fragments are generally the coarser crystalline grains in limestones, and the abundance of crinoids is generally reflected in the mean grain size of the stone.

In differential reactivity tests, the dolomites averaged 10.9 mg of  $\text{SO}_3$  per 30 mg of calcine, whereas the limestones averaged 8.5 mg of  $\text{SO}_3/30$  mg of calcine. The comparable values for the marls and chalks are 9.55 and 10.68 mg, respectively. Two of the marls had rather low differential reactivities, while another, sample 2129, had a high value (14.9 mg of  $\text{SO}_3/30$  mg of calcine). The reef dolomite, Type 5, had the highest differential reactivity (17.0) and the marble, sample 1336, the lowest (3.86). The very fine-grained limestone that contained scattered dolomite rhombs (2071) tested very low (4.42); limestone sample 2061, very similar to 2071 but lacking the dolomite rhombs, also had a very low differential reactivity. However, the fine-grained Type 4 limestone, which is similar petrographically to 2061 and 2071, had a rather high reactivity (14.0 mg of  $\text{SO}_3/30$  mg calcine). Such diversity in differential reactivities are thought to result from slight differences in pore structure of the calcines of these samples, which give rise to differences in the rate of reaction during the first few tens of seconds of exposure to  $\text{SO}_2$ . A significant difference thus results in the degree of sulfation after a reaction period of 120 seconds. Determination of the rate of reaction of calcines at a constant degree of sulfate loading enabled Borgwardt (1970b) to correlate the differential reactivity with the surface area measurements of the calcines. As the surface area of the calcine increased, a linear increase in the differential reactivity was observed for calcines that had a constant degree of sulfation.

#### Grain Size and Pore Structure Related to Sorption

Results on the nine type samples (Harvey, 1970) indicated that the  $\text{SO}_2$  capacity tended to increase with increasing pore volume and decreasing

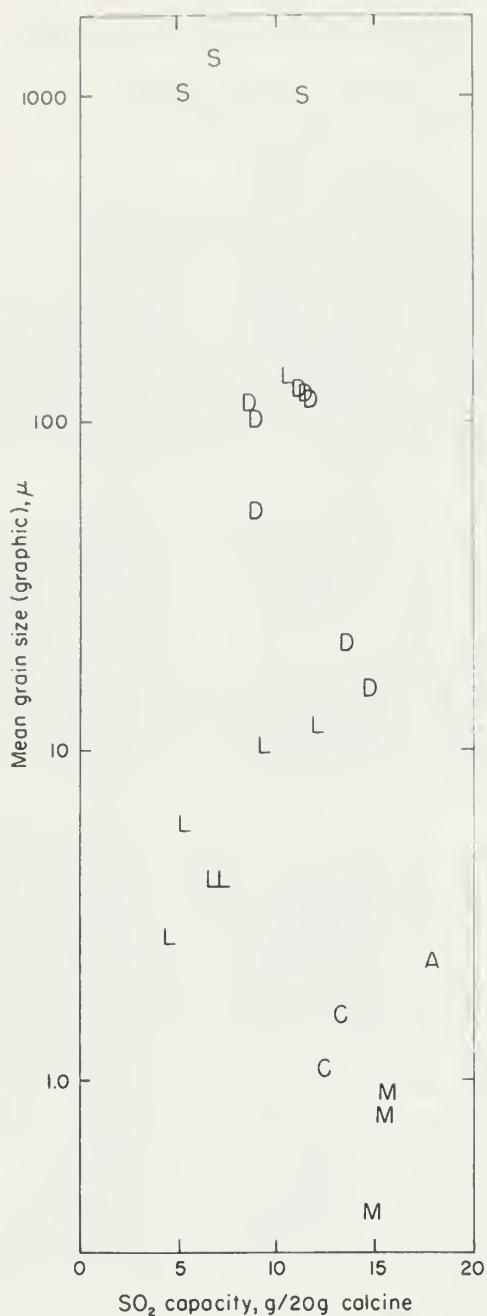


Fig. 4. SO<sub>2</sub> capacity as measured in fixed-bed tests versus mean grain size of carbonate rocks. L = limestones, D = dolomites, S = calcite spars, C = chalks, A = aragonite, and M = marls.

grain size of the stone. These relations are more conclusively demonstrated by the data on all samples studied to date, with the exception of the magnesite. Graphs of the various petrographic parameters, showing notable correlations, appear in figures 4 to 9.

The finer grained rocks in general tend to have greater SO<sub>2</sub> capacities (fig. 4). The measure of the grain size plotted is the graphic mean from tables 6 and 8; a similar distribution is apparent when the arithmetic mean is substituted for the graphic mean. In figure 4, four clusters of data points occur. The cluster of points near 10  $\mu$  are for the micritic limestones and two petrographically similar dolomites (Types 6 and 9), and shows increasing SO<sub>2</sub> capacity as grain size increases. This behavior, which is contrary to the general trend, is related to the occurrence of crinoid grains in the limestones, as discussed above. The coarse-grained crinoidal limestone (Type 3) is associated with the coarse-grained dolomites near 100  $\mu$  on the graph (fig. 4), and each of these samples contains abundant intragranular voids. The chalks and marls and the oolitic aragonite samples constitute the cluster (fig. 4) with the finest grain size and show the highest average SO<sub>2</sub> capacity of the various groups. The three coarsest samples (top of fig. 4) are calcite spar and related types. The grain size of the carbonate rocks shows no significant correlation with their differential reactivity (120-second reaction period).

Measurements of the mean QTM pore volume (tables 5 and 9) show certain correlations with SO<sub>2</sub> capacities (fig. 5). With exception of the aragonite, a chalk, and two marl samples that had QTM pore volumes thought to be erroneously low (each circled in fig. 5), there is a significant linear increase in pore volume with increasing sorption capacity. The correlation coefficient is 0.71. The pore volume (QTM) within the 2  $\mu$  to 16  $\mu$  size interval plotted against the SO<sub>2</sub> capacity (fig. 6) also shows increasing sorption capacity as pore volume increases. The 2  $\mu$  to 16  $\mu$  pore volume has a correlation coefficient of 0.97 with the QTM pore volume.

The differential reactivity data plotted against the QTM pore volume of the uncalcined samples (fig. 7) and against the pore projection (fig. 8) show

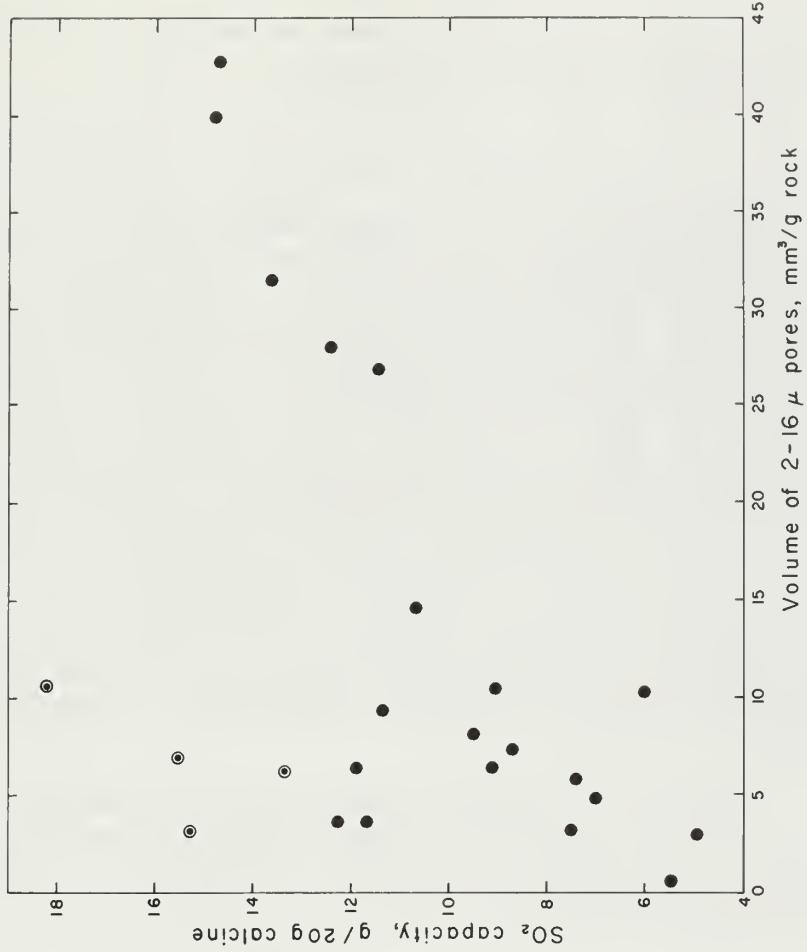


Fig. 5.  $\text{SO}_2$  capacity as measured in fixed-bed tests versus volume of pores larger than  $0.9 \mu$  in diameter (Tables 5 and 10) in carbonate rocks, determined by Quantimet methods. The pore volumes of samples that are circled are believed to be erroneously low. Correlation coefficient, disregarding circled samples, is 0.71.

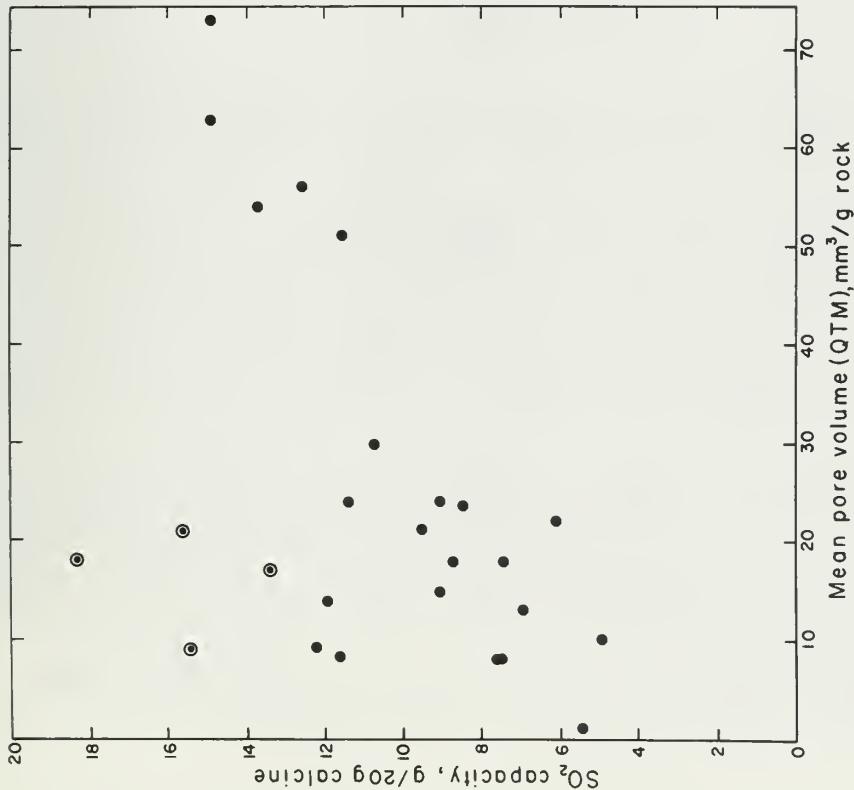


Fig. 6.  $\text{SO}_2$  capacity in fixed-bed tests versus volume of 2-16  $\mu$  pores,  $\text{mm}^3/\text{g}$  rock  
2 to 16  $\mu$  in "diameter" pores of carbonate rocks, as determined by Quantimet methods.

little significant correlation. Other petrographic properties show even less correlation with differential reactivity.

#### Chemical Analyses and Sorption

Graphic plots of the weight percentages of the chemical elements present in the samples versus the  $\text{SO}_2$  reactivities show no correlations except for the plot of the sodium content.\* The capacity to react with  $\text{SO}_2$  tends to increase with the amount of sodium (reported as  $\text{Na}_2\text{O}$ ) in the sample (fig. 9). Figure 9 shows the logarithm of  $\text{Na}_2\text{O}$  plotted against the  $\text{SO}_2$  capacity test results; the correlation coefficient is 0.78. Sodium is considered only as an index, not as a reactant with  $\text{SO}_2$ ; however, it may be acting as a catalytic or fluxing agent to produce a more reactive calcine. For all the type samples except Types 6 and 9, the sodium is thought to be in the form of soluble salts rather than inert clays; analysis shows that 77 percent of the  $\text{Na}_2\text{O}$  of Type 6 is a soluble salt, as is 97 percent of the  $\text{Na}_2\text{O}$  of Type 9. Similarly high proportions of the minor amounts of  $\text{Na}_2\text{O}$  present in the phase II samples are most likely in the form of soluble salts too. These salts are probably located along grain boundaries and in void inclusions in the dolomite samples (Lamar and Shrode, 1953). Murray (1956) reported that sodium salts of chloride and carbonate decreased shrinkage of limestone and dolomite particles during calcination.

Comparison between the two calcite spar samples (Types 1 and 2) shows that Type 2 contains the highest concentration of all trace elements (table 4). These impurities may have contributed to the higher sorption capacity observed for Type 2.

#### REACTION PRODUCTS

Fundamental differences in the reactions of calcines with  $\text{SO}_2$  were observed by analyses of the X-ray spectrum of sulfur from reacted specimens examined with the SEM (fig. 10). The  $1700^\circ \text{ F}$  calcine of Iceland spar calcite (Type 1) exposed to  $\text{SO}_2$  for 600 seconds was converted to anhydrite ( $\text{CaSO}_4$ ) only at the edges of the particles (fig. 10B), whereas under the same conditions the calcine of the coarse-grained crinoidal limestone reacted to form anhydrite throughout the particles (fig. 10D). This difference in behavior is thought to be due to differences in the porosity of calcined particles. Anhydrite was the reaction product in every reacted sample studied. No magnesium-sulfur compounds were detected in any of the samples, but periclase ( $\text{MgO}$ ) was abundant in the reacted calcines of the dolomite samples.

The anhydrite on the exterior surfaces of  $\text{SO}_2$ -reacted particles ( $3\frac{1}{2}$  hours at  $1800^\circ \text{ F}$ ) is granular, with grains ranging from about 1 to 6 microns. The particles of anhydrite are smooth surfaced, and their boundaries tend to be linear in reacted dolomites (fig. 11). Examination of the SEM micrographs of reacted Type 5 dolomite indicates a moderate number of pore channels lead

\* An insignificant correlation coefficient (0.23) was observed between the  $\text{Fe}_2\text{O}_3$  in the sample and the sorption capacity.

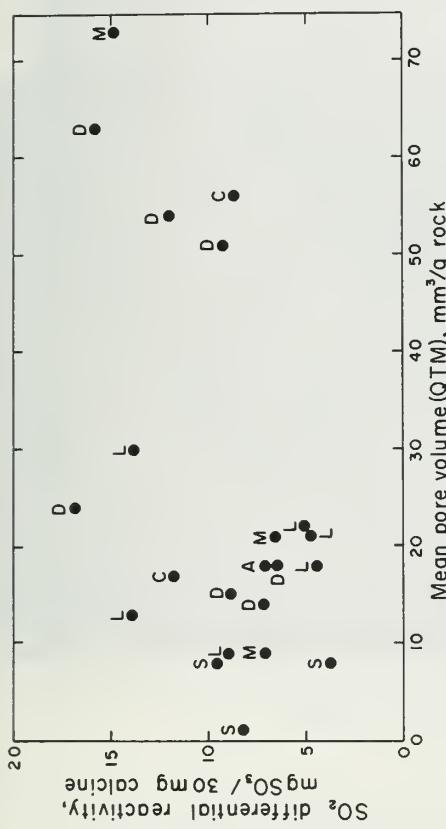


Fig. 8. SO<sub>2</sub> reactivity in differential tests versus pore (boundary) projection of carbonate rocks, as determined by Quantimet methods. L = limestone, D = dolomites, S = Iceland spar, calcite spar, and marble, C = chalks, M = marls, and A = aragonite. Correlation coefficient is 0.67.

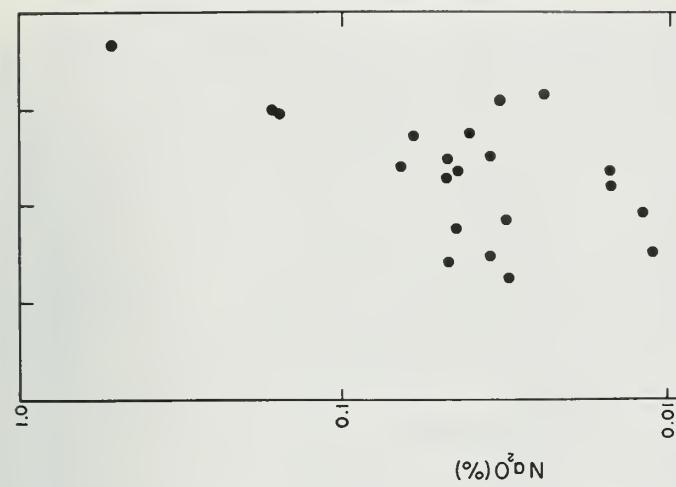


Fig. 7. SO<sub>2</sub> reactivity in differential tests versus volume of pores larger than 0.9  $\mu$  in diameter in carbonate rocks, as determined by Quantimet methods. L = limestone, D = dolomites, S = Iceland spar, calcite spar, and marble, C = chalks, M = marls, and A = aragonite. Correlation coefficient is 0.48.

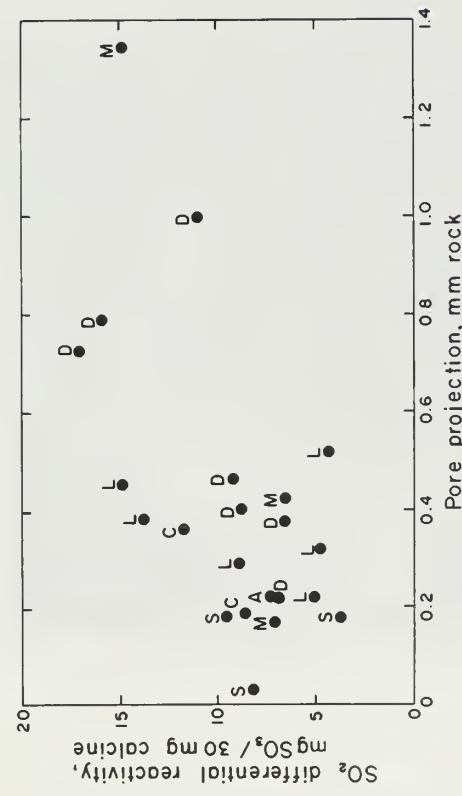


Fig. 9. SO<sub>2</sub> capacity in fixed-bed tests versus Na<sub>2</sub>O content of carbonate rocks. Correlation coefficient is 0.78.

Fig. 8. SO<sub>2</sub> reactivity in differential tests versus pore (boundary) projection of carbonate rocks, as determined by Quantimet methods. L = limestone, D = dolomites, S = Iceland spar, calcite spar, and marble, C = chalks, M = marls, and A = aragonite. Correlation coefficient is 0.67.



A. Cross section of a calcined particle of Iceland spar (type 1) reacted with  $\text{SO}_2$  for 600 seconds; embedded in epoxy. Polished section of particle is 0.67 by 0.25 mm; SEM, X120.



B. Sulfur X-ray scan of A, showing sulfated lime on outer rim.



C. Cross section of a calcined particle of coarse limestone (type 3) reacted with  $\text{SO}_2$  for 600 seconds. Polished section of particle is 0.48 by 0.25 mm; SEM, X200.



D. Sulfur X-ray scan of C, showing complete sulfate permeation.

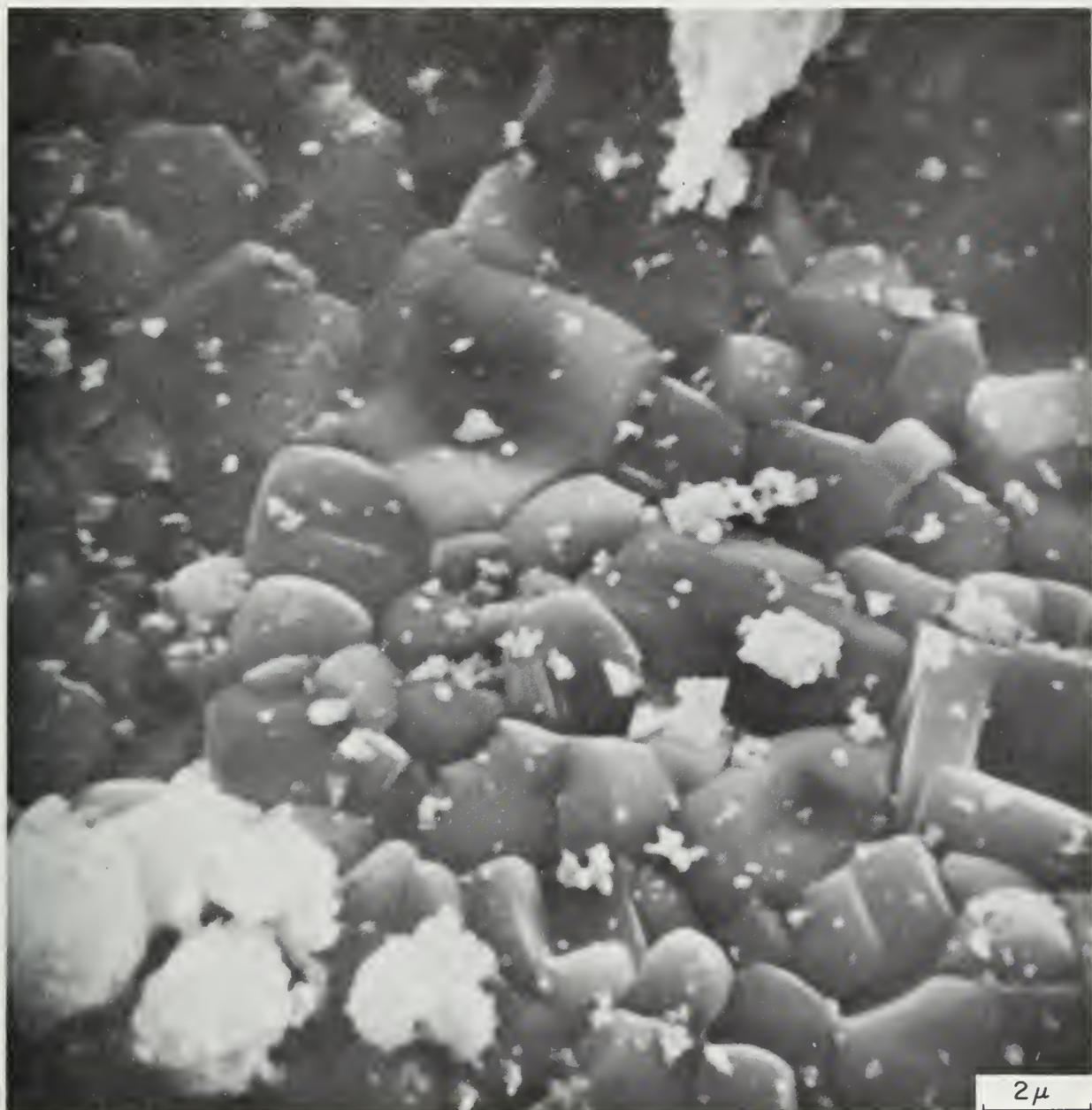


Fig. 11 - Exterior surface of  $\text{SO}_2$ -reacted calcine of a high-purity reef dolomite (type 5), showing blocky texture of anhydrite (gray). The highlighted grains are dust particles derived from the sample. SEM, X9350.

from the external surfaces into the particles. SEM studies of reacted calcines of Type 4, an example of the limestones, show larger grains (up to 30  $\mu$ ) of anhydrite that are generally smooth and anhedral and have a tightly interlocking granular fabric that is essentially impervious (fig. 12).

#### SUMMARY AND CONCLUSIONS

Petrographic properties of the various carbonate rocks observed in this study reveal correlations with the  $\text{SO}_2$  sorption capacity ( $3\frac{1}{2}$ -hr reaction period).

The pore volume of carbonate rocks appears to be an important index property to the sorption capacity of a rock. The greater the total pore volume of the carbonate rock, especially when pores are between 2 and 16  $\mu$  in diameter, the greater its capacity for reacting with  $\text{SO}_2$  in the fixed-bed tests. In support of this conclusion, the data on two porous dolomite samples show that they had high  $\text{SO}_2$  reactivity in spite of containing moderate amounts of inert clay and quartz impurities. Six high-purity dolomites, each consisting for the most part of tightly interlocking rhombic to anhedral grains of dolomite containing many intragranular voids, had an average  $\text{SO}_2$  sorption capacity of 10.3 grams per 20 grams of calcine, whereas two dolomites containing 10 to 15 percent clay and quartz had an average reactivity of 14.3 g/20 g of calcine. The pore structure of these samples appears to be more influential in their  $\text{SO}_2$  behavior than does their degree of mineral or chemical purity.

Of the limestones tested, those containing crinoidal fossil fragments had the highest  $\text{SO}_2$  sorption capacity. The positive influence of the crinoidal grains is probably due to the presence of voids within the grains that make the calcine more porous. These voids probably also contain most of the sodium-bearing soluble salts.

Comparison between the crystallographically "perfect" Iceland spar calcite (Type 1) and the calcite spar sample, which contains abundant intracrystalline voids and twin lamellae (Type 2), also supports the idea that voids have a positive influence on sorptive capacity, Type 2 having more than twice the capacity for  $\text{SO}_2$  sorption of Type 1. The pores in carbonate rocks are believed to remain as pores through the early, and possibly the middle, stages of calcination.

The grain size of carbonate rocks is also a useful index of  $\text{SO}_2$  sorption capacity. In general, the finer the grain size the higher the  $\text{SO}_2$  capacity. The coarsest grained samples—Iceland spar, calcite spar, and marble—had an average capacity of 8.2 g/20 g calcine, whereas the very fine-grained marls, chalks, and oolitic aragonite had an average capacity of 15 g/20 g. The dolomites and crinoidal limestones have intermediate sorption capacity. However, the fine-grained limestones with tightly interlocked grains have unusually low capacities.

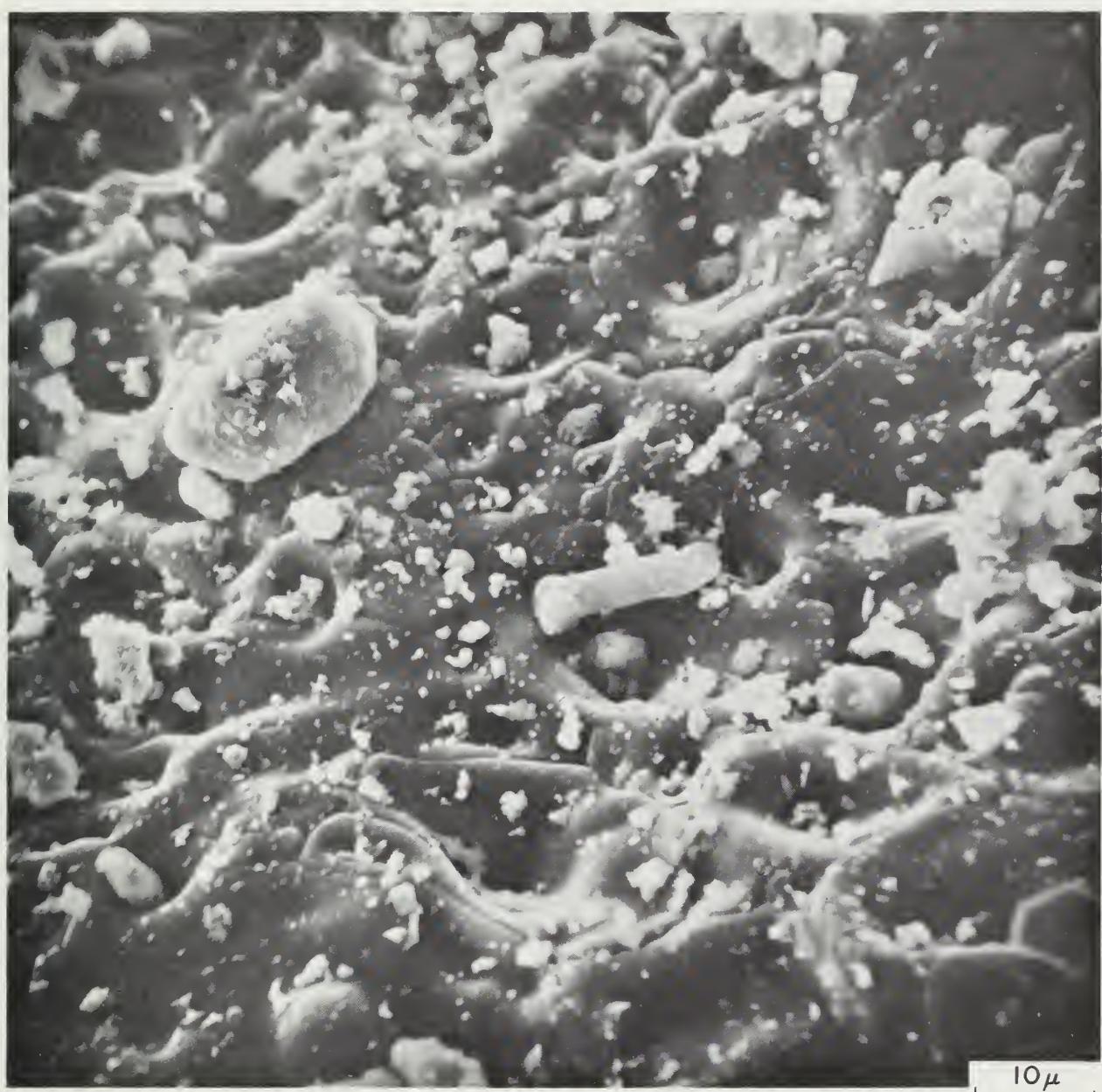


Fig. 12 - Exterior surface of SO<sub>2</sub>-reacted calcine of a fine-grained limestone (type 4), showing dense mosaic of anhedral grains of anhydrite (gray). The highlighted grains are dust particles derived from the sample. SEM, X2080

Of particular importance is the observed tendency of the samples with high sodium content to have high sorption capacities. Minor to trace amounts of sodium, frequently present in carbonate rocks as soluble salts and located along grain boundaries and in fluid inclusions within grains (Lamar and Shrode, 1953), may act as a catalytic or fluxing agent to produce a more porous calcine.

Relations between the petrographic and the differential reactivities (120-second reaction period) are not clear. Of the five high-purity dolomites that are nearly identical petrographically, four have differential reactivities ranging from 6.3 to 9.3 mg SO<sub>3</sub>/30 mg calcine. The fifth (Type 5) has a reactivity of 17.0 mg SO<sub>3</sub>/30 mg calcine. In addition, although the very fine-grained and dense limestone (Type 4) is completely different from the coarse crinoidal limestone (Type 3) in texture, their SO<sub>2</sub> differential reactivities are nearly identical. Differential reactivities are thought to result from slight differences in pore structure of the calcines that bring about changes in rate or reaction during the first few tens of seconds of exposure to SO<sub>2</sub>. These changes give rise to noticeable differences in the degree of sulfation after a reaction period of 120 seconds. Evaluation of reacted calcines at a constant degree of sulfate loading enabled Borgwardt (1970b) to correlate the differential reactivity with the surface area measurements of the calcines.

The product of the reaction of calcines of carbonate rocks with SO<sub>2</sub> in laboratory tests conducted at 1800° F was found to be anhydrite (CaSO<sub>4</sub>). Two types of reactions were observed with a scanning electron microscope equipped with an X-ray spectrum analyzer. The calcines of the nonporous Iceland spar calcite (Type 1) absorbed sulfur only on the outer surface of their particles, while the calcines of a porous limestone (Type 3) absorbed sulfur throughout their particles. This supports the conclusion that the pore structure of the rock is maintained through the reactive stage of the calcine.

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